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TITLE: ANTIREFLECTION COATING COMPOSITION CONTAINING PHOTO-ACID PRODUCING AGENT

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ABSTRACT:

PROBLEM TO BE SOLVED: To provide an antireflection film compsn., a substrate containing this compsn., and its producing method so as to obtain a resist relief image having a profile in the vertical direction with decreased footing and notching.

SOLUTION: This antireflection film compsn. consists of a resin binder, an acid producing agent or thermoreactive acid producing agent, and a

photoreactive acid producing agent. The resin binder consists of repeating
units of anthracenyl groups. and preferably contains a crosslinking agent such
as an amine-based material. It is preferable that the photoreactive acid
producing agent produces an acid by exposure to 100 to 300 nm UV rays and is
stable for exposure for one or more min at 110 to 175

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(54) ANTIREFLECTION COATING COMPOSITION CONTAINING PHOTO-ACID PRODUCING AGENT

(57)Abstract:
PROBLEM TO BE SOLVED: To provide an antireflection film compsn., a substrate containing this compsn., and its producing method so as to obtain a resist relief image having a profile in the vertical direction with decreased footing and notching.
SOLUTION: This antireflection film compsn. consists of a resin binder, an acid producing agent or thermoreactive acid producing agent, and a photoreactive acid producing agent. The resin binder consists of repeating units of anthracenyl groups. and preferably contains a crosslinking agent such as an amine-based material. It is preferable that the photoreactive acid producing agent produces an acid by exposure to 100 to 300 nm UV rays and is stable for exposure for one or more min at 110 to 175°C. The relief image of the photoresist layer is formed by (i) applying the antireflection compsn. on a substrate, (ii) applying a photoresist compsn. thereon, (iii) exposing the resist layer to produce an acid from the photoreactive acid producing agent of the antireflection compsn., and (iv) developing the resist layer.

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CLAIMS

[Claim(s)]

[Claim 1] 1) The low-reflectance-coating constituent used with the photoresist constituent which consists of a resin binder, two acid generators or a thermal reaction nature acid generator, and a 3 light reactivity acid generator compound, and is covered by the upper layer.
[Claim 2] An optical reactivity acid generator compound is a stable acid-resisting constituent according to claim 1 substantially, even if exposed to the temperature of about 110-175 degrees C more than for about 1 minute.
[Claim 3] An optical reactivity acid generator compound is an acid-resisting constituent according to claim 1 which is what generates an acid, when the deep ultraviolet of an effective dose is exposed.
[Claim 4] The acid-resisting constituent according to claim 1 with which a resin binder has an anthracenyl repeat unit.
[Claim 5] Furthermore, the acid-resisting constituent according to claim 1 which comes to contain a cross linking agent.
[Claim 6] The acid-resisting constituent according to claim 5 whose cross linking agent is the material of the amine base.
[Claim 7] The covered substrate which becomes substrate up from the substrate which has the coat layer of the acid-resisting constituent of 1 claim 1 publication, and the coat layer of two photoresists.
[Claim 8] The covered substrate according to claim 7 with which the photoresist is covered on the acid-resisting layer.
[Claim 9] A photoresist is a covered substrate according to claim 7 which is the photoresist of the positive type which consists of a resin binder and an optical reactivity acid generator compound, and which was amplified chemically.
[Claim 10] The optical reactivity acid generator compound of an acid-resisting constituent and the optical reactivity acid generator compound of a photoresist are a covered substrate according to claim 7 which both generates an acid compound of the same kind substantially, when activation radiation is exposed.
[Claim 11] The optical reactivity acid generator compound of an acid-resisting constituent and the optical reactivity acid generator compound of a photoresist are a covered substrate according to claim 7 which both generates the same acid compound, when activation radiation is exposed.
[Claim 12] The optical reactivity acid generator compound of an acid-resisting constituent and the optical reactivity acid generator compound of a photoresist are a covered substrate according to claim 11 which generates both sulfonic acids, when activation radiation is exposed.
[Claim 13] The covered substrate according to claim 8 whose substrate is a micro electronic wafer, a flat-surface panel-display substrate, or an optical electronic substrate.
[Claim 14] The covered substrate which consists of a substrate which has the coat layer of the acid-resisting constituent which does not contain a cross-linking-agent component in essence on a substrate including 1 resin binder and an optical reactivity acid generator compound, and the coat layer of two photoresists.
[Claim 15] (a) How to form the relief image of a photoresist which consists of applying on a substrate the layer of the acid-resisting constituent which consists of an optical reactivity acid generator compound, applying the layer of (b) photoresist constituent on an acid-resisting constituent layer, exposing the (c) photoresist layer according to activation radiation, generating an acid from the optical reactivity acid generator compound of an acid-resisting constituent, and developing the photoresist layer by which (d) exposure was carried out.
[Claim 16] The method according to claim 15 of carrying out heat hardening of the acid-resisting layer, before applying a photoresist constituent layer.
[Claim 17] The method according to claim 16 by which the optical reactivity acid generator of an acid-resisting constituent is not substantially activated in the heat hardening of an acid-resisting layer.
[Claim 18] The method according to claim 15 by which a relief latent image is formed in a photoresist layer of the aforementioned exposure of a photoresist layer.
[Claim 19] The method according to claim 15 by which an acid-resisting constituent layer is not exposed before exposure of the photoresist layer by activation radiation by the radiation which activates an optical reactivity acid generator.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the constituent which decreases reflection by back track of the exposure irradiation light to the photoresist layer (overcoatedphotoresistlayer) by which soil coating was carried out from the substrate. this invention relates to the acid-resisting covering constituent containing the optical reactivity acid generator compound (photoacidgenerator compound) which decreases the footing (footing) or notching (notching) of a photoresist relief image by which coat formation was carried out, and which is not desirable more at a detail.
[0002]
[Description of the Prior Art] A photoresist is a film used in order to imprint a picture to a substrate. The enveloping layer of a photoresist is formed on a substrate and, subsequently this photoresist layer is exposed by the source of irradiation activated through the photo mask. This photo mask has another transparent field to an opaque field and the activated irradiation to the activated irradiation. If the activated irradiation is exposed, a photoresist coat will produce the chemical denaturation (photoinduced chemical transformation) by which induction was carried out to light, and the substrate by which the photoresist was coated with the pattern of a photo mask by it will imprint. Development of a photoresist acquires after exposure the relief picture in which alternative processing of a substrate is possible.
[0003] A positive type or a negative mold is also possible for a photoresist. In the case of most negative-mold photoresists, the portion of the photoresist enveloping layer exposed by the activated irradiation performs a polymerization or bridge formation in the reaction between the photosensitive compound of a photoresist constituent, and the reagent in which the polymerization of a photoresist constituent is possible. Therefore, it is hard coming to dissolve the exposed covering portion in a development solution rather than the portion which is not exposed. It is harder coming to dissolve in development the field which becomes easier to dissolve the portion which was exposed in the case of the positive type in a development solution, and is not exposed by contrast on the other hand. The photoresist constituent is well-known to this contractor. "The photoresist material and the method (photoresist Materials and Prosesses)" () by De Forest (Deforest) [McGraw Hill Book Company,] [New] " York, Chapter 2 of 1975, and Molly (Moreay) Semiconductor lithography, It is indicated by a principle, Chapter 2 of material (Semiconductor Lithography, Principles Practices and Materials, Plenum Press, New York), and Chapter 4. Set to this invention about a photoresist constituent, its process, and a usage about both this reference. It is illuminating ** 3.
[0004] in semiconductor manufacture, the main uses of a photoresist come out and there are, and since one of the purposes makes the function as a circuit discover the flake of semiconductors ground highly, such as silicon or gallium arsennide, it is changing into the complicated matrix of the electronic conduction path of a desirable a micron or submicron geometric pattern It is a key for suitable photoresist processing attaining this purpose. Although strong interdependence is among various photoresist processing processes, in acquiring the photoresist picture of high resolution, exposure is considered to be one of the more important processes.
[0005]
[Problem(s) to be Solved by the Invention] Reflection of the activated irradiation light which is often used in order to expose a photoresist may present the limit of the resolution of the picture patternized in the photoresist layer. If irradiation light reflects from a substrate / photoresist interface, the irradiation intensity in the photoresist between exposure may change, and the line breadth of a photoresist will become uneven by it at the time of development. Since irradiation light is scattered about to the photoresist field which is not made into the purpose of exposure from a substrate / photoresist interface, line breadth will vary also in this case. Generally, the grade of dispersion or reflection is various by the field, and line breadth becomes uneven also by this.
[0006] Moreover, reflection of the activated irradiation (light) is known by this contractor as a "stationary wave effect" (standingwave effect). In order to lose the influence of the chromatic aberration of the lens of an aligner, with photoresist projection technology (photoresistprojection techniques), the homogeneous light or a quasi-monochromatic light is usually used. However, if the homogeneous light or a quasi-monochromatic light is used for photoresist exposure, a useful interference and a detrimental interference will become remarkable especially by the irradiation light reflex in a photoresist / substrate interface. In such a case, the reflected light interferes with an incident light and forms a stationary wave in the interior of a photoresist. Since the stationary wave of a large amplitude makes the film of the photoresist of a underexposure

in the minimum wave, in the case of the large substrate field of reflection nature, a problem becomes still more serious. The layer of a underexposure starts the problem (edge acuity problems) of edge radicalization in a photoresist picture, and checks the perfect development of a photoresist. Since all the exposures taken to expose if the amount of a photoresist increases increase, the time taken to expose a photoresist serves as a function which usually increases to the thickness of a photoresist. However, the exposure time contains further the harmony-element which changes between maximum and the minimum values with the thickness of a photoresist for the stationary wave effect. Since line breadth will be changed when the thickness of a photoresist is uneven, a problem becomes still more serious.

[0007] Furthermore, change of the fine structure (substrate topography) of a substrate also generates the problem (resolution-limiting reflection problems) of the reflection to which resolution is reduced. Invasion of the irradiation light by various dispersion or reflection in the direction which is not controlled will produce every picture on a substrate, and the heterogeneity of the development of a photoresist will be caused. The influence of the reflected light becomes still more important as the fine structure of a substrate becomes still more complicated, in order to design a more complicated circuit. For example, especially since the metal connection used by many microelectronics substrates is the field of the fine structure and high reflection nature, it poses a problem.

[0008] From the latest inclination which is high-density, there is movement which shortens wavelength of the source of exposure to far-ultraviolet (DUV) light (wavelength of 300nm or less) and KrF excimer laser light (248.4nm), ArF excimer laser light (193nm), an electron beam, and a soft X ray in the industrial world. Since the wavelength which shortened the photoresist coat at the imaging **** sake was used, generally reflection increased from on the resist front face like the front face of the substrate which serves as the base as a result. Therefore, using shorter wavelength has enlarged the problem of the reflection from a substrate front face. By another technique used in order to lessen the problem of the reflected light, the irradiation optical-absorption layer inserted between a substrate front face and a photoresist enveloping layer has been used. For example, an acid-resisting (antihalation) constituent and its usage are indicated by the PCT application public presentation official report 90th / No. 03598 (WO 90/03598), the EPO application public presentation official report No. (0639 EP, A1, 941) 0639941 and U.S. Pat. No. 4,910,122, 4,370,405, and 4,362,809. In the aforementioned reference, as for such a layer, an acid-resisting layer or ARC (acid-resisting constituent) is expressed. The very useful antihalation (acid resisting) constituent which changes from a resin binder and a cross-linking-agent compound to the European Patent application public presentation official report No. (EP, A1,542,008) 542008 of a cypripedium rhe company (Shipley Co.) is indicated.

[0009]

[Means for Solving the Problem] this invention offers the suitable new optical-absorption constituent for the use as a low-reflectance-coating constituent, especially application to deep ultraviolet (deep UV). The acid-resisting constituent of this invention consists of an optical reactivity acid generator which can generally mitigate notching and the footing of a resin binder and the relief image of the photoresist by which coat formation was carried out which are not desirable.

[0010] It is thought that it is very tended that the base mixed from the substrate or acid-resisting constituent coat layer in the lower layer of a resist layer is neutralized the acid produced from the optical reactivity acid generator of a photoresist, especially especially the strong acid of optical generating of a resist amplified chemically. Moreover, when an acid is spread to the acid-resisting constituent coat layer in a lower layer, the acid of optical generating from a resist layer will be lost. Loss of an acid makes the resolution of the developed resist layer fall in either neutralization or diffusion. Such diffusion or the typical influence by the neutralization process is that a footing or notching arises in the base section of the resist relief image of the part to which the acid concentration of optical generating fell most remarkably.

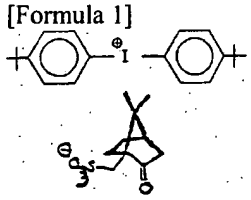
[0011] The acid of sufficient amount for an acid-resisting constituent layer can be generated during exposure of a resist layer, ensuring avoiding loss of this acid from a resist layer, and making the acid of an effective dose exist in the whole direction of resist layer thickness by making an optical reactivity acid generator mix in the acid-resisting constituent coat layer by which the paint film was carried out to the fundus according to this invention. That is, diffusion or neutralization of the acid from a resist layer can be stabilized by existence of the acid of optical generating by the inside of an acid-resisting constituent layer, and an acid-resisting constituent / resist layer interface. as a result, there is almost a footing or notching -- it is -- the resist relief image which has the profile of the perpendicularly it is not can be manufactured Please refer to the result of the below-mentioned example and the example of comparison about this.

[0012] When constructing a bridge in the acid-resisting constituent of this invention, as for the optical reactivity acid generator of an acid-resisting constituent, it is desirable not to be substantially activated during bridge formation of an acid-resisting constituent. After PAG (optical reactivity acid generator) is activated about the acid-resisting constituent over which a bridge is especially constructed by heating, PAG of an acid-resisting constituent should be substantially stable on crosslinking reaction conditions so that an acid may be generated during exposure of the resist layer covered by the upper layer. Specifically, even if exposed to about 140 or the temperature of 150-190 degrees C for about 5 - 30 minutes, or more than it, as for PAG, it is desirable not to decompose substantially or not to denaturalize.

[0013] As for the optical reactivity acid generator of an acid-resisting constituent, in some [at least] acid-resisting constituents of this invention, it is desirable that it acts as a surfactant and can condense near the upper part of the acid-resisting constituent which approached most the acid-resisting constituent / resist coat layer interface. For example, it is better [this good] and that in which PAG has the aliphatic machine of wide senses, such as a basis fluorine-ized [machine / ARUKENIRU / of C2-15 / the substitution or the unsubstituted alkyl group beyond carbon numbers 6-15 or it or an alicyclic

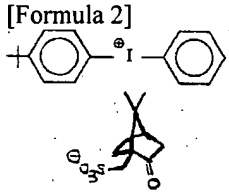
machine, 1, the alkyl group of C1-15 which have two or more fluorine substituents preferably, or] preferably four or more carbon numbers, is mentioned.
[0014] Since it is activated by exposure by ********** (about 248nm and/or about 193nm), an acid-resisting constituent can be effectively used especially for especially the desirable optical reactivity acid generator of an acid-resisting constituent of this invention with the photoresist of the deep ultraviolet covered by the upper layer. Being activated on the same exposure wavelength is suitable for the optical reactivity acid generator of an acid-resisting constituent, and the optical reactivity acid generator of a photoresist constituent. Moreover, in order to ensure that the optical reactivity acid generator of the both sides of an acid-resisting constituent and a photoresist constituent is activated on single exposure wavelength, the sensitizer material blended with a photoresist constituent and/or an acid-resisting constituent can be used.
[0015] Furthermore, when the acid-resisting constituent of this invention is made to expose with activation radiation during irradiation of a photoresist layer, it is desirable to use it together with the photoresist constituent with which the optical activity compound of the optical activity compound of an acid-resisting constituent and a photoresist constituent generates the same or almost same acid compound (optical product), i.e., the optical product which has the same acid strength as the same desirable diffusion property. When the acid-resisting constituent and the product of the acid by each light of a resist were alike as mentioned above, it was checked that the resolution of the relief image of the resist covered by the upper layer improves further. the acid-resisting constituent and the product of the acid by the light of a resist which here, "are substantially the same" -- the PKa value (it measures at 25 degrees C) of these two optical products -- the maximum -- small -- there is only a difference of about 2 or 2.5 and the PKa values of two optical products are preferably few -- only 1.5 differs from about 1 but it means that the PKa value of two optical products has only small the difference in about 0.75 still more preferably Furthermore, the acid-resisting constituent and the product of the acid by the light of a resist which "are substantially the same" have slight molecular weight, or it is suitable for them that there is only about 40% of difference, and it is preferably different only about 20%, and is still more preferably different only about 15%. As for an acid-resisting constituent and the optical product of a resist, it is still more desirable respectively that both optical products are sulfonic acids, or both sides are the acids of the same kinds, such as halo acids, such as HBr.
[0016] The desirable acid-resisting constituent of this invention contains the resin binder containing 1 or the chromophore component beyond it which can reduce reflection by absorbing the chromophore in the resist constituent covered by the upper layer by which exposure radiation is carried out, i.e., exposure radiation. For example, in the desirable acid-resisting constituent used, an anthracenyl group etc. is mentioned as a desirable chromophore with the photoresist of deep ultraviolet (DUV). The anthracenyl alkyl ester which has the side chain radical expressed with a general formula-(C=O) O(CH2) n-anthracene (n in a formula is 1 - about 6 integer) especially is desirable. As other desirable chromophores, nuclear-substitution KINORINIRU derivatives, such as a quinolinyl group, and hydronalium KISHIKINORI nil, phenan training nil, an acridine machine, are mentioned. Preferably, it consists of the chromophores more desirable [about 10 - 60% of] and above about 5 to 90% of the repeat unit of a resin.
[0017] The desirable resin binder of this invention has the optical density of about 4 units / mu at least on exposure wavelength (for example, 193nm or 248nm). Moreover, hydroxy **** of a resin has the desirable resin binder in which things "which were done for SUSUKU", and which react with a cross-linking-agent component by the part, such as ester which can generate the aforementioned reactant basis under existence of a carboxy portion, an acid, or others, are possible, for example. The desirable resin binder of an acid-resisting constituent which has a chromophore component is a copolymer, and is manufactured by the polymerization of two or more [in which at least one monomer contains a chromophore machine] different monomers. Offering a remarkable advantage made this composition clear to adding and organic-functions-izing a chromophore machine to the polymer formed beforehand.
[0018] Moreover, it is desirable to contain the acid or thermal reaction nature acid generator which induces or promotes 1 of an acid-resisting constituent or bridge formation of the component beyond it in **** of the acid-resisting constituent in this invention. Generally, desirable bridge formation of an acid-resisting constituent consists of a cross-linking-agent component which became [material / of the amine bases, such as glycouril, benzoguanamine, and melamine resin,] independent. Especially, a glycouril resin is desirable and the available powder link 1174 is especially desirable from an American cyanamide company.
[0019] The acid-resisting constituent of this invention is used combining the photoresist constituent of the positive type amplified chemically most preferably. Moreover, the acid-resisting constituent of this invention is suitable to use it with the photoresist of a negative mold not only a resist positive type [other] but. Furthermore, this invention offers the new product which consists of the method of forming the relief image of a photoresist, and a substrate with which only the acid-resisting constituent of this invention was covered combining the photoresist constituent. Other modes of this invention are indicated below.
[0020]
[Embodiments of the Invention] The acid-resisting constituent of this invention consists of one sort or the optical reactivity acid generator beyond it (namely, "PAG") with suitable using notching and the footing of a photoresist layer which are covered by the upper layer and which are not desirable in prevention or sufficient amount preventing substantially. The suitable amount of PAG can be changed by quite large width of face, and can be easily defined based on experience. Generally, PAG beyond one sort or it of the acid-resisting constituent of this invention is suitably used to the whole quantity of an acid-resisting constituent in the amount not more than about 0.25 - 5 % of the weight, or it. Please refer to the

below-mentioned example about the concrete amount used.
[0021] Moreover, especially the amount of desirable PAG of an acid-resisting constituent changes according to the property and processing conditions of a photoresist which are used with an acid-resisting constituent. For example, if a photoresist produces the optical product of an acid with the comparatively strong optical reactivity acid generator of a photoresist by exposure after-backing attachment (PEB) by low temperature comparatively, a possibility of pyrolyzing in this PEB of subsequent low temperature will not not much have an acid formation object by the light of an acid-resisting constituent, and the acid in an acid-resisting constituent will serve as comparatively more high effective concentration. Therefore, an optical reactivity acid generator can be effectively blended with this acid-resisting constituent by comparatively low concentration. On the contrary, when using the photoresist by which exposure after-backing attachment is comparatively carried out at an elevated temperature, some acid formation objects by the light of an acid-resisting constituent become that it is easy to be pyrolyzed from after that. In such a case, an optical reactivity acid generator can be blended with an acid-resisting constituent by comparatively high concentration, the acid generated by light can be secured to effective concentration, and the maximum fall of the footing which is not desirable can be carried out.
[0022] A sulfonate compound is desirable PAG in the acid-resisting constituent of this invention, and especially its sulfonate is desirable. A desirable compound is PAGI and PAG2 which are expressed with the following chemical formula concretely.
[0023]
[Formula 1]



1

[0024]
[Formula 2]



2

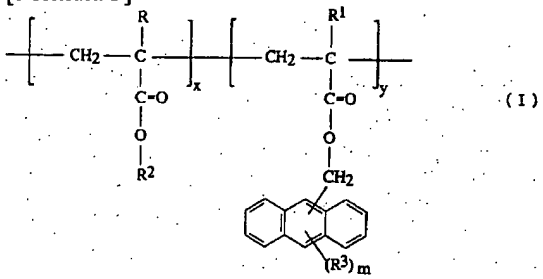
[0025] The synthesis method of Above PAGI can manufacture such a sulfonate compound according to the publication of the below-mentioned example 2 indicated in detail. The sulfonate of the above PAG 2 can be manufactured by the same method as an example 2 except making t-butylbenzene and benzene of an equimolecular amount react in the first stage together with an acetic anhydride and KIO3 mostly.
[0026] The ester and the sulfonyl oxyketones which were sulfonated are mentioned as other suitable sulfonate of PAG. Please refer to "journal OBU photopolymer science and technology (J. of Photopolymer Science and Technology), and 4(3):337-340" by which the suitable sulfonate of PAG which includes benzoin tosylate, alpha-(p-toluenesulfonyloxy) acetic-acid t-buthylphenyl, and alpha-(p-toluenesulfonyloxy) acetic-acid t-butyl is indicated (1991). Moreover, the desirable sulfonate of PAG is indicated by U.S. Pat. No. 5,344,742 specifications, such as a sinter (Sinta).
[0027] Moreover, an onium salt can be used as an optical reactivity acid generator in the acid-resisting constituent of this invention. The suitable thing made clear especially the onium salt that is a weak parent nature anion. As an example of the aforementioned anion, the metal of 2 - 7 **, such as B, P, and As, or the halogen complex of a nonmetallic anion is mentioned, for example to Sb, Sn, Fe, Bi, aluminum, Ga, In, Ti, Zr, Sc, D, Cr, Hf, and Cu row. as the example of a suitable onium salt -- the [of periodic tables, such as diaryl diazonium salt, and a halo NIUMU salt / for example, /, quarternary-ammonium-salt, phosphonium salt, arsonium salt, aromatic sulfonium salt, and sulfoxonium salt, a selenium salt,] -- the [Va, Vb group, and] -- the onium salt of Ia, Ib group, and the Ith group is mentioned The example of a suitable and desirable onium salt can be seen on U.S. Pat. No. 4,442,197; 4,603,101 and 4,624,912 specifications.
[0028] A nitrobenzyl ester homolog, s-triazine derivative, etc. are mentioned as other useful acid generators in the acid-resisting constituent of this invention. The acid generator of suitable s-triazine is indicated by for example, the U.S. Pat. No. 4,189,323 specification.
[0029] Moreover, in the acid-resisting constituent of this invention, the compound which generates an acid by the light of non-ionicity by which the degree was halogenated is also suitable. For example, 1 and 1-screw (p-chlorophenyl) - 2, 2, and 2-trichloroethane (DDT), 1 and 1-screw (p-methoxypheny) - 2, 2, and 2-trichloroethane, 1, 2, 5, 6, 9, 10-hexa BUROMO cyclo decane, 1, 10-dibromo decane, A 1 and 1-screw (p-chlorophenyl) -2, 2-dichloroethane, 4, and 4-dichloro-2-TORIKURORO methyl benzhydrol (KERUTAN), A hexa chloro dimethyl sulfone, a 2-chloro-6-TORIKURORO methylpyridine, o and o-diethyl-o-(3, 5, 6-TORIKURORO-2-pyridyl) phosphoro thio NETO, 1, 2, 3, 4, 5, 6-hexachlorocyclohexane, N-[1, and 1-screw (p-chlorophenyl) - 2, 2, a 2-trichloroethyl] acetamide, It is the compound of the tris (2, 3-dibromopropyl) isocyanurate, 2, and 2-screw (p-chlorophenyl) -1, 1-dichloroethylene, tris (TORIKURORO methyl)-s-triazine and these isomers, an analog, a homolog, and the remainder.

[0030] Moreover, the suitable optical reactivity acid generator also for the Europe patent application public presentation No. 0164248 and a 0232972 specification is indicated. As an acid generator desirable to deep ultraviolet exposure, it is [- 2, 2, and 2-TORIKURORO ethanol, tris (1, 2,, 3-methane sulfonyl) benzene, TORISUTORIKURORO methyl triazine etc. are mentioned.] 1 and 1-screw (p-chlorophenyl). - It is 2, 2, and 2-trichloroethane (DDT), 1, and 1-screw (p-methoxy phenol). - It is 2, 2, and 2-trichloroethane, 1, and 1-

[0031] As mentioned above, it is thought that the resin binder component in the acid-resisting constituent of this invention absorbs reflection effectively in a deep ultraviolet field (typically about 100-300nm) preferably. As mentioned above, as for a resin binder, it is desirable to contain the chromophore unit of deep ultraviolet, i.e., the repeat unit which absorbs deep ultraviolet. Generally the part which carried out conjugate combination highly is a suitable chromophore. 2-3 pieces, the condensed ring which it has four pieces, or a polycyclic formula machine is the chromophore of usually desirable deep ultraviolet about the ring which the aromatic machine of a polynuclear hydrocarbon or a heterocycle formula, for example, one ring, is 3 - 8 member ring, and has 0-3 N, O, or S atoms to each ring especially. As such a chromophore, nuclear-substitution quinolinyl groups, such as substitution and an unsubstituted phenan tolyl group, substitution and an unsubstituted anthra sill machine, substitution and an unsubstituted acridine machine, substitution and an unsubstituted naphthyl group, substitution and an unsubstituted quinolinyl group, and a hydroxy quinolinyl group, etc. are mentioned. Especially, substitution and an unsubstituted anthra sill machine are desirable. For example, as for a resin binder, it is desirable to have an anthra sill machine in a side chain, and its acrylic resin expressed especially by the following general formula (I) is desirable.

[0032]

[Formula 3]



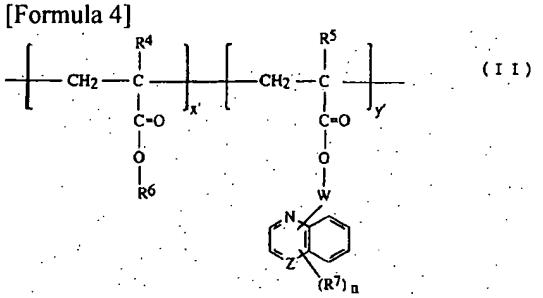
(I)

[0033] the inside of a formula, and R and R1 -- it -- a hydrogen atom, substitution or the unsubstituted carbon number 1 - about 8 alkyl group are shown, and substitution or the alkyl group of unsubstituted C1-unsubstituted C6 is desirable it independently Each R2 shows substitution or the unsubstituted carbon number 1 - about 10 alkyl group, and, more generally shows independently a carbon number 1 - about 6 alkyl group. each R3 -- becoming independent -- a halogen atom (especially F, Cl, Br), a carbon number 1 - about 8 alkyl group, a carbon number 1 - about 8 alkoxy group, and carbon-number 2- the ARUKENIRU machine of about 8, a carbon number 2 - about 8 alkynyl group, a cyano group, a nitro group, etc. are shown m is the integer of 0-9 (when all anthra sill rings are replaced by the hydrogen atom), and is 0, 1, or 2 preferably. x is the mole ratio or percent of an alkyl acrylate unit in polymer, and is about 10 - 80% of abbreviation preferably. y is the mole ratio or percent of an anthracene unit in polymer, and is about 5-10 to 90% preferably. moreover -- although other monomeric units may be contained as long as polymer is a request -- an anthracene unit -- at least -- about ten-mol % -- containing is desirable A hydroxyalkyl machine is especially desirable R2 set, and its alkyl group in which R2 has a first-class hydroxyl group like 2-hydroxyethyl (-CH2CH2OH) especially is desirable. 9-(methylene) anthracene ester unit is preferably contained to a resin binder.

[0034] Another desirable resin binder consists of the substitution, the unsubstituted quinolinyl group, or KINORINIRU derivative which has one piece or the ring atom of N, O, or S beyond it like a hydroxy quinolinyl group. Polymer may contain other units, such as a carboxy which branched from the frame, and/or an ester unit. Especially the desirable resin binder of an acid-resisting constituent is acrylic polymer expressed with the following general formula (II).

[0035]

[Formula 4]



(II)

[0036] Among a formula, respectively, R4 and R5 show a hydrogen atom, substitution or the unsubstituted carbon number 1 - about 8 alkyl group, and substitution or its alkyl group of unsubstituted C1-unsubstituted C6 is desirable independently. Each

R6 shows substitution or the unsubstituted carbon number 1 - about 10 alkyl group, and, more generally shows independently a carbon number 1 - about 6 alkyl group. W shows single bond, substitution, or the alkylene machine of the unsubstituted carbon number 1 - abbreviation 4, and its single bond is desirable. Z shows carbon, nitrogen, oxygen, or a sulfur atom. each R7 -- becoming independent -- a halogen atom (especially F, Cl, Br), a carbon number 1 - about 8 alkyl group, a carbon number 1 - about 8 alkoxy group, and carbon-number 2- the ARUKENIRU machine of about 8, a carbon number 2 - about 8 alkynyl group, a cyano group, a nitro group, etc. are shown n is the integer of 0-7 (when all rings are replaced by the hydrogen atom), and is 0, 1, or 2 preferably. x' is the mole ratio or percent of an alkyl acrylate unit of polymer, and is about 10 - 80% of abbreviation preferably. y' is the mole ratio or percent of KINORINIRU in polymer, or a hydronalium KISHIKINORI nil unit, and is about 5 - 90% of abbreviation preferably. moreover -- although other monomeric units may be contained as long as polymer is a request -- KINORINIRU and/or a hydronalium KISHIKINORI nil unit -- at least -- about ten-mol % -- containing is desirable A hydroxyalkyl machine is especially desirable R6 set, and its alkyl group in which R6 has a first-class hydroxyl group like 2-hydroxyethyl especially is desirable.

[0037] Each basis (basis R1-R7 replaced, W, and the replaced PAG substituent are included) by which the above was replaced may be replaced by one piece or the suitable basis beyond it in 1 or the replaceable position beyond it. this -- carbon-number 2- which has the alkanoyl machine represented with alkanoyl machines of C1-C6, such as a halogen atom (especially F, Cl, Br), a cyano group, a hydroxyl group, a nitro group, and an acyl group, for example, a carbon number 1 - about 8 alkyl group, one piece, or a unsaturated bond beyond it as a suitable basis -- the ARUKENIRU machine of about 8 and an alkynyl group, a carbon number 1 - about 6 alkoxy group, etc. are mentioned

[0038] The resin binder in the acid-resisting constituent of this invention is preferably compounded by the polymerization of two or more sorts in which at least one sort of monomers contain the chromophore machine of an anthracenyl group, a quinolinyl group, or a hydroxy quinolinyl group of different monomers. For example, the isolation radical polymerization by the reaction of two or more monomers which are about 70 degrees C or more in an inert atmosphere (nitrogen or argon) and heating temperature preferably, and provide the bottom of existence of a radical initiator with various polymerization units although reaction temperature changes with the boiling points of the reactivity of each reagent to be used or a reaction solvent (when using a solvent) is adopted suitably. Please refer to the below-mentioned example 1 about a concrete reaction condition. Based on the publication of this specification, this contractor can define the suitable reaction temperature of each system easily based on experience.

[0039] A reaction solvent can be used if needed. As a suitable solvent, aromatic solvents, such as alcohols, such as propanol and butanols, and benzene, a chlorobenzene, toluene, a xylene, etc. are mentioned. Dimethyl sulfoxide, a dimethylformamide, and THF are also suitable. Moreover, a non-solvent can also perform polymerization reaction. Various kinds of isolation radical initiators are used for manufacture of the copolymer of this invention. For example, azo compounds, such as the azo-screw -2, 2'-isobutyronitrile (azobisuisobutironitoriru), and a 1 and 1'-azo-screw (cyclohexane carbonitrile), are used. A peroxide, peroxy-acid ester, a peroxy acid, and a persulfate can also be used. Moreover, although it is not so desirable, you may organic-functions-ize the resin formed beforehand in a chromophore unit. For example, glycidyl phenol resin, such as a glycidyl novolak, can be made to react with an anthranil carboxylic acid.

[0040] The resin binder in the acid-resisting constituent of this invention shows absorptivity preferably good on the deep ultraviolet wavelength in the field of 100 - 300nm of abbreviation. More specifically, the desirable resin binder of this invention has 3 extinction unit /mu on the exposure wavelength (for example, about 248nm or about 193nm) used, and it has about four to 16 or more optical density of an extinction unit / mu on the wavelength exposed preferably at least at about five to 20 or more extinction units /mu, and the exposure wavelength used more preferably. By raising the rate of the chromophore unit on a resin, each resin can give a high extinction value.

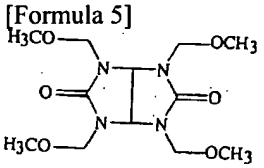
[0041] the resin binder expressed with the aforementioned general formula (II) -- weight average molecular weight (Mw) -- about 1,000- about 10,000,000dalton -- more -- general -- about 5,000- the molecular weight of about 1,000,000dalton, and number average molecular weight (Mn) -- about 500- it is desirable to have the molecular weight of about 1,000,000dalton this invention -- the molecular weight (either Mw or Mn) of the polymer to kick is suitably measured by the gel permeation chromatography

[0042] Although the resin binder of the acid-resisting constituent which has the chromophore of the above-mentioned extinction nature is generally desirable, the acid-resisting constituent of this invention may also contain other resins as either an auxiliary resin or a single resin binder component. For example, phenol resin, such as poly (vinyl phenol) and a novolak, can be used. This resin is concretely indicated by the Europe patent application EP No. 542008 of a cypripedium rhe company. Moreover, other below-mentioned resins can be used for the resin binder component in the acid-resisting constituent of this invention as a photoresist resin binder.

[0043] The concentration of the resin binder component in the acid-resisting constituent of this invention may reach far and wide comparatively. More generally a resin binder is used by about 60 - 90% of the weight of the concentration of all dryness components (all components except solvent support) 50 - 95 % of the weight of abbreviation of all the dryness components in an acid-resisting constituent.

[0044] Moreover, the bridge formation type acid-resisting constituent in this invention contains a **** agent component. Various kinds of cross linking agents containing the cross linking agent of the acid-resisting constituent currently indicated concretely can be used for the Europe application EP No. 542008 of the aforementioned cypripedium rhe company as reference. For example, the cross linking agent of the amine bases, such as melamine material containing melamine resin

which is manufactured at an American cyanamide (American Cyanamid) company and is marketed as a cross linking agent of a suitable acid-resisting constituent by the brand name of Cymel (Cymel) 300, 301, 303, 350, 370, 380, 1116, and 1130, is mentioned. The glycouril which includes available glycouril from an American cyanamide company especially is desirable.
[0045] The material of benzoguanamine and the urea base is also a suitable resin. As this resin, a benzoguanamine resin available from an American cyanamide company at the brand name of Cymel 1123 and 1125 and a urea-resin available from an American cyanamide company at the brand name of beetles (Beetle) 60, 65, and 80 are mentioned. Whether the copolymer and formaldehyde of an acrylamide or methacrylamide other than such commercial elegance are made to react in an alcoholic content solution, N-alkoxy methylacrylamide, or methacrylamide cannot be, but the resin of the above-mentioned amine base can be manufactured from copolymerization of ** and other suitable monomers.
[0046] Especially the cross linking agent of the acid-resisting constituent in which weak base like methoxymethyl-ized glycouril is shown is desirable. A desirable cross linking agent is methoxymethyl-ized glycouril corresponding to the following general formula (III) concretely.
[0047]
[Formula 5]



(III)

[0048] This methoxymethyl-ized glycouril can be manufactured by the well-known method. These compounds are also marketed from the American cyanamide company by the brand name of the powder link (Powderlink) 1174.
[0049] Especially polyfunctional compounds, such as a phenyl which a hydroxy compound is mentioned and has the hydroxyl group or hydroxyalkyl substituent like a hydroxyalkyl substituent of C1-C8 beyond one piece or it as a suitable **** agent which shows other weak base, or other aromatic compounds, are suitable. Generally phenol nature compounds, such as a dimethanol phenol [C6H3(CH2OH)2OH], and other compounds replaced by the position where the hydroxyl group and the hydroxyalkyl substituent adjoined (to inside of 1 - 2 ring atom), a phenyl replaced by the position where it has the nuclear-substitution methanol machine or other hydroxyalkyl machines beyond one piece or it, and at least one hydroxyl group adjoined the above-mentioned hydroxyalkyl substituent especially or an aromatic compound, are desirable.
[0050] The cross linking agent which shows weak base, such as methoxymethyl-ized glycouril used for the acid-resisting constituent of this invention, can give the outstanding lithography performance characteristic of reducing remarkably notching or the footing of a relief image of a photoresist covered by the upper layer (SEM inspection). Generally the cross-linking-agent component in the acid-resisting constituent of this invention is 5 - 50% of the weight of the amount of the total solid (all components except solvent support) of an acid-resisting constituent, and, more generally exists in about 7 - 25% of the weight of the amount of a total solid.
[0051] As for the bridge formation acid-resisting constituent of this invention, it is still more desirable to include bridge formation for catalyst-izing, the acid to promote, or a thermal reaction nature acid generator compound during hardening of the coat layer. Preferably, a thermal reaction nature acid generator, i.e., the compound which generates an acid by heat-treatment, is used. As a thermal reaction nature acid generator, various kinds of well-known compounds, such as 2, 4, 4, 6-tetrabromo cyclohexa JIENON, benzoin tosylate, 2-nitrobenzyl tosylate, and other organic sulfonic-acid alkyl ester, are used suitably, for example. Generally the compound which generates a sulfonic acid with activation is suitable. Generally a thermal reaction nature acid generator exists more preferably in an acid-resisting constituent by about 2% of the weight of the concentration of all dryness components 0.1 - 10 % of the weight of abbreviation of all the dryness components.
[0052] Moreover, you may only blend not a thermal reaction nature acid generator but an acid into an acid-resisting constituent as mentioned above. Especially in an acid-resisting constituent with the need of heating in case it hardens under existence of an acid so that an acid may not promote the reaction which is not desirable as for a constituent component before use of an acid-resisting constituent, that is right. As a suitable acid, strong acid or such mixture, such as sulfonic acids, such as toluenesulfonic acid and a sulfonic acid, and a 3 fluorine acid, are mentioned, for example.
[0053] Moreover, this invention includes the acid-resisting constituent over which a bridge is not constructed so notably, while meaning use of a photoresist constituent. Although this non-cross-linking acid-resisting constituent contains an optical reactivity acid generator as described above, it is not necessary to make the cross-linking-agent component, acid, or thermal reaction nature acid generator which induces or promotes crosslinking reaction contain. namely, -- this common non-cross-linking acid-resisting constituent -- a cross-linking-agent component and/or a thermal reaction nature acid generator -- essential -- not existing (that is, about 1 - 2 or less % of the weight) -- or it can be said that it does not exist completely
[0054] The acid-resisting constituent of this invention can contain further the color compound which absorbs the radiation used in order to expose the photoresist layer covered by the upper layer again. There is a surface lubricating agent (surface levelimgagent) in the additive suitably used for others, for example, a lubricating agent available from Union Carbide, the surfactant FC171 available from a three em (3M) company, or FC431 is mentioned by the brand name of Silwet (Silwet) 7604.
[0055] In order to prepare a liquefied coat constituent (liquid coating composition), the component of an acid-resisting constituent is dissolved in a suitable solvent. As a solvent, for example besides an ethyl lactate, 2-methoxy ethyl ether

(JIGURI), One sort or the glycol ethers beyond it, such as an ethylene glycol monomethyl ether and a propylene glycol monomethyl ether; Methoxybutanol, The solvent which has an ether portion and hydroxyl-group portions, such as an ethoxy butanol, methoxy propanol, and ethoxy propanol; Methyl-cellosolve acetate, Ester, such as ethylcellosolve acetate, propylene-glycol-monomethyl-ether acetate, and dipropylene-glycol monomethyl ether acetate; other solvents, such as a dibasic acid ester, propylene carbonate, and gamma-butyrolactone, are mentioned. It will depend for the concentration of the dryness component in a solvent on some factors, such as the method of application. Generally, the solid content of an acid-resisting constituent is in about 0.5 - 20% of the weight of the range of the total weight of an acid-resisting constituent, and is in about 2 - 10% of the weight of the range of the total weight of an acid-resisting constituent preferably.

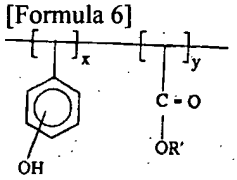
[0056] Various kinds of photoresist constituents containing the constituent which generates an acid by the light of a positive type and a negative mold with the acid-resisting constituent of this invention can be used. Generally the photoresist used with the acid-resisting constituent of this invention consists of an optical active ingredient represented with a resin binder and an optical reactivity acid generating compound. A photoresist resin binder has the functional group which enables development in alkali solution to the formed resist constituent preferably.

[0057] As mentioned above, especially the desirable photoresist used with the acid-resisting constituent of this invention is a resist amplified chemically, and is the resist constituent of the positive type amplified especially chemically. In such a constituent, the acid activated by the light in a resist layer induces the deprotection type reaction of one sort or the constituent component beyond it, and a solubility difference is given between the exposure field of a resist coat layer, and a non-exposing field.

[0058] The resist constituent amplified chemically [many] is U.S. Pat. No. 4,968,581; 4,883,740; 4,810,613; 4,491,628 and this **. It is indicated by the No. 5,492,793 specification and these all have made reference concretely about the method of preparation and the usage of a resist of a positive type which were amplified chemically. Especially the desirable photoresist that is used with the acid-resisting constituent of this invention and that was amplified chemically consists of a mixed component with the resin binder which makes a constituent the copolymer containing both an optical reactivity acid generator, phenol unit, and non-phenol unit. For example, one desirable basis of the above-mentioned copolymer has a basis unstable in an acid essentially or completely substantially only in the non-phenol unit of a copolymer. Especially one of the desirable copolymer binders has the repeat unit x and y, and it is expressed with the following general formula (IV).

[0059]

[Formula 6]



(IV)

[0060] A hydroxyl group may exist in o in a copolymer, m, or any of the p-th place among a formula. R' shows substitution or the unsubstituted carbon number 1 - about 18 alkyl group, and, more generally shows about six to 8 alkyl group from a carbon number 1. Generally t-butyl is desirable R'. One sort or the halogen atom beyond it (especially F, Cl, Br), the alkoxy group of C1-8, the ARUKENIRU machine of C2-8, etc. may replace by R' machine suitably. Unit x and y may exist by alternation regularly among a copolymer, or may be scattered at random in a copolymer.

[0061] The aforementioned copolymer can be formed easily. For example, substitution or unsubstituted alkyl acrylate, such as vinyl phenols and t-butyl acrylate, can be made to condense under well-known isolation radical conditions in the field concerned in the resin expressed with the above-mentioned general formula. The part of the replaced ester part, i.e., R'O-C(=O)-, and an acrylate unit acts on an acid as an unstable basis in a resin, if the coat layer of the photoresist containing a resin is exposed, will be guided to the acid by the photolysis and will cleave. a copolymer -- desirable -- about 8,000- about 50,000 -- it has about 15,000 - about 30,000 Mw more preferably, and molecular weight distribution are about two or less more preferably about three or less

[0062] Moreover, the copolymer of alkyl acrylate, such as non-phenol resin, for example, t-butyl acrylate, or t-butyl methacrylate, and vinyl alicyclic compounds, such as vinyl norbornyl or a vinyl cyclohexanol, can also be used as a resin binder in the constituent of this invention. The above-mentioned copolymer can be manufactured by the aforementioned isolation radical polymerization or other well-known methods again, and, probably, has about 8,000 - about 50,000 Mw, and about three or less molecular weight distribution suitably. The resist of the desirable positive type amplified chemically is further indicated by the U.S. patent No. 5,258,257 specifications, such as a sinter.

[0063] Moreover, the acid-resisting constituent of this invention is used with the resist of other positive types, such as a thing containing the resin binder containing polar functional groups, such as a hydroxyl group or a carboxylate machine, and a resin binder is used in amount sufficient in alkali solution to enable development of a resist in a resist constituent. Generally a desirable resist resin binder is phenol resin which includes gay - of gay - of a well-known phenolaldehyde condensate and ARUKE nil phenols, a copolymer, and N-hydroxyphenyl-melamines, and a copolymer in the field concerned as a novolak resin.

[0064] Moreover, the copolymer containing a phenol and a non-aromaticity ring type alcoholic unit is the desirable resin binder of the resist in this invention, and can be suitably manufactured by the partial hydrogenation of a novolak or the poly (vinyl phenol) resin. The use in the above-mentioned copolymer and a photoresist constituent is indicated by U.S. Pat. No.

5,128,232 specifications, such as SAKKEREI (Thackeray). If the desirable resist constituent of a negative mold used with the acid-resisting constituent of this invention contacts an acid, it will consist of mixture of hardening, bridge formation, or the material and the optical reactivity acid generator that becomes hard.
[0065] Especially the desirable resist constituent of a negative mold consists of resin binders, such as phenol resin, a cross-linking-agent component, and an optical active ingredient of this invention. The above-mentioned constituent and its use are indicated by U.S. Pat. No. 5,128,232 specifications, such as the Europe patent application No. 0164248 and a 0232972 specification, and SAKKEREI. As desirable phenol resin used as a resin binder component, a novolak which was mentioned above, and poly (vinyl phenol) are mentioned. As a desirable cross linking agent, the material of the amine bases, such as material of a melamine, glycouril, and the benzoguanamine base and material of the urea base, is mentioned. Especially, generally a melamine formaldehyde resin is the most desirable. This cross linking agent is commercially available, for example, melamine resin is marketed from the American cyanamide company by the brand name of Cymel 300, 301, and 303. A glycouril resin is the brand name of Cymel 1170, 1171, and 1172 and the powder link 1174, the material of the urea base is the brand name of beetles 60, 65, and 80, and a benzoguanamine resin is the brand name of Cymel 1123 and 1125, and is marketed from the American [it / it] cyanamide company.
[0066] U.S. Pat. No. 4,442,197 by which concrete reference is made as a suitable photoreaction nature acid generator compound of the resist used with the acid-resisting constituent of this invention; sulfonate photoreaction nature acid generators, such as non-ionicity organic light activity compounds, such as a halogenation light activity compound like a publication, and sulfonated ester and sulfo NIROKISHI ketones, etc. are mentioned in U.S. Pat. No. 5,128,232 specifications indicated by 4,603,101 and the 4,624,912 specification, such as an onium salt and SAKKEREI. Suitable sulfonate PAG, such as benzoin tosylate, alpha-(p-toluene sulfo NIROKISHI) acetic-acid t-buthylphenyl, and alpha-(p-toluene sulfo NIROKISHI) acetic-acid t-butyl, "please refer to journal OBU photopolymer science and technology (J. of Photopolymer Science and Technology) 4(3):337-340 (1991). Desirable sulfonate PAG is indicated by U.S. Pat. No. 5,344,742 specifications, such as a sinter, again. The aforementioned camphor sulfonate 1 and PAG 2 is a desirable optical reactivity acid generator in the acid-resisting constituent of this invention, especially the resist constituent used with the resist to which sensitization was carried out chemically [this invention].
[0067] Moreover, in the photoresist used with the acid-resisting constituent of this invention, you may contain other materials. For example, as other proper additives, a photochemistry color and a contrast color, a striation generating inhibitor, a plasticizer, a print-speed improver, etc. are mentioned. Generally the above-mentioned additive blended suitably exists by remarkable low concentration in a photoresist constituent except the bulking agent which exists as opposed to all the dryness components of a resist in the comparatively high-concentration amount of 5 - 30 % of the weight, or a color.
[0068] The acid-resisting constituent of this invention which contains a weak basic cross linking agent like suitable glycouril is useful especially for the photoresist which generates the optical product of strong acid, such as a 3 fluorine acid, camphor sulfonate, other sulfonic acids, or an acid of others which have about two or less pKa value (25 degrees C), by exposure. It is thought that the acid-resisting constituent of ******** of this invention is especially effective for the resist of the above-mentioned strong acid without being bound by the theory. Because, the grade which the strong acid of optical generating shifts from a resist, and remains in an acid-resisting constituent layer is from a low as compared with the analogous acid-resisting constituent containing a more basic cross linking agent. That is, the weak basic cross linking agent in this invention does not have a small deer length stop in the strong acid of optical generating of the resist layer covered by the upper layer as compared with the more basic cross linking agent of an acid-resisting constituent. As a result, a little loss of the acid from a resist layer will not be generated, therefore the trouble of resolution called a footing will become still smaller.
[0069] On the occasion of use of the acid-resisting constituent of this invention, an acid-resisting constituent is applied to a substrate as a coat layer, and may be applied by ******, such as spin coating, or the method of becoming. Generally an acid-resisting constituent is preferably applied on a substrate in the range whose thickness at the time of dryness is about 0.02-0.5 micrometers, and the range whose thickness at the time of dryness is about 0.04-0.20 micrometers. As long as a substrate is used suitable for the processing in connection with a photoresist, what substrate is sufficient as it. For example, let a substrate be the micro electronic wafer of silicon, a silicon dioxide, or an aluminum-aluminum oxide. Moreover, the substrate of a gallium arsenide, a ceramic, a quartz, or copper can also be used. The substrate used for the application of a liquid crystal display or other flat-surface panel displays, for example, a glass substrate, the substrate with which the indium-stannic-acid ghost was covered are used suitably. Light and the substrate for optical electronic instruments (for example, waveguide) can also be used.
[0070] Preferably, before a photoresist constituent is applied on an acid-resisting constituent, an acid-resisting layer is hardened. Hardening conditions change by the component of an acid-resisting constituent. For example, a curing temperature and conditions will become more intense compared with the case of the constituent containing an acid or an acid generator compound, when an acid or a thermal reaction nature acid generator is not contained in a constituent. General hardening conditions are for about 0.5 - 40 minutes at about 120 degrees C - 225 degrees C. As for hardening conditions, it is desirable to insolubilize an acid-resisting constituent coat layer substantially to the developer of a photoresist solvent and an alkaline-water solution.
[0071] A photoresist is applied to an acid-resisting constituent front face after the above-mentioned hardening. A photoresist can be applied like the case of an application of this acid-resisting constituent by all common use meanses, such as spin, being immersed, a meniscus, or roll coating. Following an application, generally, preferably, a solvent is removed and a photoresist

coat layer is dried by heating until a resist layer serves as the set to touch. It must not be most desirably generated on the mixture ****** essence target of an acid-resisting constituent layer and a photoresist layer.
[0072] A resist layer is formed by activation radiation through a mask after that by the method of common use. Exposure energy is amount sufficient by a part of acid-resisting constituent layer thickness [at least] so that the acid generated by light from PAG of an acid-resisting constituent may exist in an acid-resisting constituent layer / resist coat layer interface to activate a photoreaction nature acid generator while forming the image which activated the optical active ingredient of a resist system effectively, and was patternized by the resist coat layer. Generally, exposure energy is in the range represented by about three to 300 mJ/cm2, and it depends for it on the approach of an exposure device, each resist, and the resist to adopt in part. Generally, sufficient amount to carry out optical activity of the effective dose of an acid to a lower layer acid-resisting constituent layer is required for the exposure adopted as general imaging of a resist layer.
[0073] The exposed resist layer is turned to exposure after-backing attachment processing if needed, and produces a solubility difference between the exposure field of a coat layer, and a non-exposing field, or enlarges the difference. For example, in the acid hardening photoresist of a negative mold, in order to make the crosslinking reaction promoted with an acid induce, generally it is necessary to carry out exposure afterbaking. Moreover, in the resist of many positive types amplified chemically, in order to make the deprotection reaction promoted with an acid induce, it is necessary to carry out exposure afterbaking. Generally, exposure after-backing attachment processing conditions are more specifically in an about 50 degrees C - 160 degrees C temperature requirement including the temperature of about 50 degrees C or more.
[0074] The exposed resist coat layer is developed with the developer of basic solution, such as inorganic alkali preferably illustrated after that with hydroxylation tetrabutylammonium, a sodium hydroxide, a potassium hydroxide, a sodium carbonate, a sodium bicarbonate, a specific silicate, a specific metasilicate, an aqueous ammonia solution, etc. An organic developer can be used apart from this. Generally, development is performed according to the method of well-known technology. Following development, final baking of an acid hardening photoresist performed for several minutes at the temperature of about 100-150 degrees C is often adopted, and hardens further the coat layer field developed and exposed.
[0075] or [that the developed substrate **********s chemically the substrate field which appeared in the photoresist according to the method of common knowledge of after that, for example, the field concerned,] -- or it plates and these substrate field top that appeared in the photoresist is processed alternatively As a suitable etching means, there are an etching solution of a hydrofluoric acid, plasma-gas etching of oxygen plasma etching etc., etc. The anti-halation coat layer over which the bridge was constructed by plasma-gas etching is removed.
[0076]
[Example] In addition, all the reference described previously is quoted by this specification. Moreover, although the following examples explain this invention concretely, this invention is not limited to these examples.
[0077] Example 1 The methacrylic-acid hydroxyethyl (HEMA) / methyl anthracene methacrylate (ANTMA) copolymer of the manufacture aforementioned general formula (I) of the desirable resin binder of an acid-resisting constituent were manufactured as follows. HEMA16.0g (0.1229 mols) distilled and refined to the 3 TSU mouth round bottom flask of 300ml capacity equipped with a magnetic agitator, a capacitor, nitrogen, and the suction entrance, methyl anthracene methacrylate 8.49g (0.0307 mols), azobisuisobutironitoriru0.2449g (1 % of the weight), and THF180ml were taught. The reaction flask was quenched in liquid nitrogen, purging with nitrogen. When the contents of a reaction flask froze, the flask was exhausted, and subsequently it purged 3 times with nitrogen. Then, it flowed back for 18 hours, stirring reaction mixture. After settling the polymer of the obtained yellow white in the 3000ml ether and filtering it, it dried at 50 degrees C under the vacuum, and the HEMA/ANTMA copolymer was manufactured. 86% of yield. this copolymer -- a -CH2C(CH3)-(COOCH2CH2OH)-unit -- 81-mol % and a -CH2C(CH3)-(COOCH2-9-anthracene)-unit -- 19-mol % -- it had, and Mw was 2295, Mn was 19150, and Tg was 101 degrees C
[0078] Example 2 The manufacture above PAG 1 of JI (4-t-buthylphenyl) iodonium (+/-)-10-camphor sulfonate is manufactured as follows. That is, 214.00g [of potassium iodates] (1.00 mols) and t-butylbenzene 268.44g (2.00 mols) and 408.36g (4.00 mols) of acetic anhydrides were taught to the three-lot round bottom flask of 21 capacity. The flask is equipped with the equalization tap funnel which was fixed to the upper part and with which it used and the selfish paddle agitator, the thermometer, and the nitrogen gas discharge pipe were fixed. Reaction mixture was cooled at 10 degrees C by the iced water bath, and while 215.78g (2.20 mols) of concentrated sulfuric acids was dropped by another funnel, it added. This addition was performed at the speed which maintains reaction temperature at about 25 degrees C, and 2 hours was required. With advance of addition, white suspension changed to the orange gradually at first. When addition was completed, reaction mixture was stirred at the room temperature (20 degrees C) for further 22 hours. Reaction mixture was cooled at 5-10 degrees C, and while 600ml water was dropped over 30 minutes, maintaining temperature at 30 degrees C or less, it added (it should add at a low speed so that early generation of heat may especially be suppressed, and about 75ml of the beginning may add the remaining water comparatively quickly after that). This mixture that became muddy was washed 3 times by hexane 100ml in the separation funnel of 21 capacity (in order to remove unreacted t-butylbenzene and some 4-t-butyl iodobenzene by-products), and sulfuric-acid hydrogen diaryl iodonium solution was moved to the reaction container of 31 capacity.
[0079] After adding 232.30g (1.00 mols) of -10-camphor sulfonic acids at once, cooling and agitating a solution at 5-10 degrees C (+/-), the solution was neutralized by 620ml (9.20 mols) of ammonium hydroxides. When the amount of the used base assumed that the reaction advanced quantitatively, it was the amount of theory taken to neutralize the full-acid kind in a container. Addition of a base was performed at speed which maintains the temperature of 25 degrees C or less, and about 1

hour was required. When pH of the reaction mixture near the addition end was set to about 7, crude diaryl iodonium camphor sulfonate precipitated as a yellowish brown solid. This suspension was stirred at the room temperature for 3 hours, and PAG material was separated as follows. That is, after washing once by 200ml (14.8 Ns NH4OH 5 ml+H2O 195ml) of 2.5wt% rare ammonium hydroxides, it rinsed twice by 200ml of water, and pH was set to about 7, until carried out suction filtration of the yellowish brown solid, collected them, it took them out in the state where it became wet, it added to the dichloromethane 11 and pH of a washing object became the range of 7-8. After drying with magnesium sulfate, it distilled off under reduced pressure of a dichloromethane, the residue was further dried at 50 degrees C under the vacuum for 16 hours, and 390.56g of yellowish brown solid-like rough products was obtained. Subsequently the solid of the obtained yellowish brown color was recrystallized and refined by the following method.

[0080] The yellowish brown solid was dissolved in the reflux isopropanol (about 375g PAG is contained all over about 1150ml IPA) of the minimum amount in 2l. round bottom flask of capacity, and the solution of a homogeneous low red heat was obtained. This heat solution was moved to the conical flask of 2l. capacity, was changed, and it cooled. While this solution was still warm, when hexane 500ml was added, the crystal generated immediately after it. It cooled to the room temperature and the crystallized mixture was held for 4 hours. It washed twice by 200ml (it prepared by cooling solvent mixture by the dry ice-acetone bath before use) of 1:3 mixed solvents of a very cold isopropanol-hexane until it carried out suction filtration, it collected solids and it became white, after cooling the crystallized solution at about 5 degrees C for 1.5 hours using an iced water bath. The white solid was dried under the vacuum by the aspirator for 1 hour until PAG [JI (4-t-buthylphenyl) iodonium (+/-)-10-camphor sulfonate] was separated as white powder been smooth. 285g PAG is obtained in this stage. 2nd recrystallization can be carried out by the same method.

[0081] Next, manufacture, its use, and the example of comparison of examples 3 and 4 and the examples 1A, 1B, and 2 of comparison, i.e., the acid-resisting constituent of this invention, are described.

[0082] The desirable acid-resisting constituent of this invention was prepared by mixing the component shown in the example 3 following. In addition, the amount of components expresses "%" of a rate to the total weight of a liquefied low-reflectance-coating constituent.

1) Resin binder : polymer (hydroxyl-group portion.) It reaches about 4% of replaced glycidyl groups. About 80% of a hydroxyl group -O(C=O) CH2-9-ANTORASE The novolak-resin base replaced by N 2.17% two cross-linking-agents: -- powder link 1174(American cyanamide company) 0.61% three acids: -- p-toluenesulfonic acid 0.06% light [4] reactivity acid generator : G t-butyl diphenyliodonium camphor SURUHONE - TO 0.16% five surfactants: -- FC171 (3M company) 0.03%6 solvent: -- ethyl lactate 18% cyclohexanone 10% Propylene glycol monomethyl ether Spin coating of the acid-resisting constituent was carried out on 68.97% single-crystal-silicon substrate with a diameter of 100mm, and it printed on the bottom of a vacuum for 60 seconds at 175 degrees C on the hot platen. The obtained thickness was 600A. The hot platen was commercially applied to 7950A in thickness after calcinating for 60 seconds at 135 degrees C for the available positive-type photoresist (marketed from the cypripedium rhe company by the brand name of UVIIHS) of DUV under the vacuum on this acid-resisting constituent layer. ISI The resist layer which carried out KrF excimer irradiation (wavelength of 248nm) by the exposure of 12.0 mJ/cm2 through the mask patternized in the thin line and the small gap, and was covered with the XLS projection stepper by the upper layer was exposed. Subsequently, after printing a wafer on the bottom of a vacuum for 90 seconds at 130 degrees C on a hot platen, negatives were developed for 60 seconds with CD-26 developer (cypripedium rhe company; alkaline-water solution). The footing of a resist was measured in the cross section SEM (scanning electron microscope) about both the isolated line with a width of face of 0.25 micrometers and the high density line, and it was an average of 3nm.

[0083] Except having removed the example of comparison 1A photoreaction nature acid generator, the acid-resisting constituent was prepared like the above-mentioned example 3. Spin coating of this acid-resisting constituent was carried out on the single-crystal-silicon substrate with a diameter of 100mm, and it printed on the bottom of a vacuum for 60 seconds at 205 degrees C on the hot platen. The obtained thickness was 600A. The hot platen was commercially applied to 7950A in thickness after calcinating for 60 seconds at 135 degrees C for the available positive-type photoresist (marketed from the cypripedium rhe company by the brand name of UVIIHS) of DUV under the vacuum on the above-mentioned acid-resisting constituent layer. ISI The resist layer which carried out KrF excimer irradiation (wavelength of 248nm) by the exposure of 10.5 mJ/cm2 through the mask patternized in the thin line and the small gap, and was covered with the XLS projection stepper by the upper layer was exposed. Subsequently, after printing a wafer on the bottom of a vacuum for 60 seconds at 130 degrees C on a hot platen, negatives were developed for 60 seconds with CD-26 developer (cypripedium rhe company; alkali solution). The footing of a resist was measured in the cross section SEM about both the isolated line with a width of face of 0.25 micrometers and the high density line, and it was an average of 39nm.

[0084] It replaced with the diphenyliodonium camphor sulfonate PAG of the example of comparison 1B example 3, and the acid-resisting constituent was prepared like the above-mentioned example 3 except having used N-(perfluoro-1-octane sulfo NIROKISHI)-5-norbornene -2 and 3-dicarboxymide. In addition, N-(perfluoro--1-octane sulfonyloxy)-5-norbornene -2 and 3-dicarboxymide are more unstable than diphenyliodonium camphor sulfonate with heat, and are decomposed at about 150 degrees C. Spin coating of this acid-resisting constituent was carried out on the single-crystal-silicon substrate with a diameter of 100mm, and it printed on the bottom of a vacuum for 60 seconds at 175 degrees C on the hot platen. The obtained thickness was 600A. The hot platen was commercially applied to 7950A in thickness after calcinating for 60 seconds at 130 degrees C for the photoresist (marketed from the cypripedium rhe company by the brand name of UVIHS) of an available

DUV positive type under the vacuum on the above-mentioned acid-resisting constituent layer. ISI The resist layer which carried out KrF excimer irradiation (wavelength of 248nm) by the exposure of 12.0 mJ/cm2 through the mask patternized in the thin line and the small gap, and was covered with the XLS projection stepper by the upper layer was exposed. Subsequently, after printing a wafer on the bottom of a vacuum for 90 seconds at 135 degrees C on a hot platen, negatives were developed for 60 seconds with CD-26 developer (cypripedium rhe company; alkaline-water solution). The footing of a resist was measured in the cross section SEM about both the isolated line with a width of face of 0.25 micrometers and the high density line, and it was an average of 17nm.

[0085] The desirable acid-resisting constituent of this invention was prepared by mixing the component shown in example 4 pan below. In addition, the amount of components expresses "%" of a rate to the total weight of a liquefied low-reflectance-coating constituent.

1) Resin binder : 9-anthryl methyl methacrylate (26-mol %) and 2 - KOPORI with hydroxyethyl methacrylate (74-mol %) MA 2.48% two cross-linking-agents: -- powder link 1174(American cyanamide company) 0.36% three acids: -- p-nitrobenzyi tosylate 0.04% photoreaction [4] nature acid generator : G t-butyl diphenyliodonium camphor SURUHONE -TO 0.04% five surfactants: FC431 (3M company) 0.03% six solvents: Propylene glycol monomethyl ether 97.05%. [0086] Spin coating of the above-mentioned acid-resisting constituent was carried out on the single-crystal-silicon substrate with a diameter of 100mm, and it printed on the bottom of a vacuum for 60 seconds at 175 degrees C on the hot platen. The obtained thickness was 605A. The hot platen was commercially applied to 8620A in thickness after calcinating for 60 seconds at 135 degrees C for the available positive-type photoresist (marketed from the cypripedium rhe company by the brand name of UVIIHS) of DUV under the vacuum on this acid-resisting constituent layer. ISI The resist layer which carried out KrF excimer irradiation (wavelength of 248nm) by the exposure of 11.0 mJ/cm2 through the mask patternized in the thin line and the small gap, and was covered with the XLS projection stepper by the upper layer was exposed. Subsequently, after printing a wafer on the bottom of a vacuum for 90 seconds at 130 degrees C on a hot platen, negatives were developed for 60 seconds with CD-26 developer (cypripedium rhe company; alkaline-water solution). The footing of a resist was measured in the cross section SEM about both the isolated line with a width of face of 0.25 micrometers and the high density line, and it was about 12nm of averages.

[0087] Except having removed the example of comparison 2 photoreaction nature acid generator, the same combination constituent as the above-mentioned example 4 was prepared. Spin coating of this combination constituent was carried out on the single-crystal-silicon substrate with a diameter of 100mm, and it printed on the bottom of a vacuum for 60 seconds at 175 degrees C on the hot platen. The obtained thickness was 600A. The hot platen was commercially applied to 7950A in thickness after calcinating for 60 seconds at 135 degrees C for the available positive-type photoresist (marketed from the cypripedium rhe company by the brand name of UVIHS) of DUV under the vacuum on the above-mentioned acid-resisting constituent layer. ISI The resist layer which carried out KrF excimer irradiation (wavelength of 248nm) by the exposure of 10.8 mJ/cm2 through the mask patternized in the thin line and the small gap, and was covered with the XLS projection stepper by the upper layer was exposed. Subsequently, after printing a wafer on the bottom of a vacuum for 60 seconds at 130 degrees C on a hot platen, negatives were developed for 60 seconds with CD-26 developer (cypripedium rhe company; alkaline-water solution). The footing of a resist was measured in the cross section SEM about both the isolated line with a width of face of 0.25 micrometers and the high density line, and it was an average of 27nm.

[0088] Please do not pass over the above publication to mere explanation of this invention, but unless you separate from the range or pneuma of this invention shown in the claim, understand that it can be made to be able to change variously or can also make it change.

[Translation done.]